International Journal of Trend in Scientific Research and Development (IJTSRD)
Volume 7 Issue 3, May-June 2023 Available Online: www.ijtsrd.com e-ISSN: 2456 – 6470

Sonocatalytic Performance of Fe_3O_4 Cluster Microspheres/Gratiphic Carbon Composite for Efficient Degradation of Organic Dyes

Xuan Sang Nguyen

Environmental Engineering Institute, Viet Nam Maritime University, Haiphong, Vietnam

ABSTRACT

$Fe_3O_4/g\text{-}C_3N_4$ composite was synthesized using hydrothermal simple and facile techniques. The sonocatalytic activity of the magnetic $Fe_3O_4/g\text{-}C_3N_4$ composite was studied through the H_2O_2-assisted system for degradation of water soluble organic pollutants such as methylene blue (MB), rhodamine B (RhB) and methyl orange (MO). X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped were employed for the characterizing the structure and morphology of the so-synthesized nanohybrid. The integration of H_2O_2 and catalyst dosage enhaced the sonocatalytic degradation of dyes. Furthermore, the magnetic property of the sample leaded to easier separation of the microhybrid, made it recyclable with a negligible decline in the dye degradation even after four consecutive recycles.

KEYWORDS: *Cluster sphere Fe_3O_4; sonocatalytic; composite; dye degradation*

How to cite this paper: Xuan Sang Nguyen "Sonocatalytic Performance of Fe_3O_4 Cluster Microspheres/Gratiphic Carbon Composite for Efficient Degradation of Organic Dyes" Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-7 | Issue-3, June 2023, pp.605-610, URL: www.ijtsrd.com/papers/ijtsrd57418.pdf

IJTSRD57418

1. INTRODUCTION

Recently, the development of many industries are widely using organic dyes that are among new chemicals. Large amount of production and extensive applications of organic dyes make a lot of toxic industrial wastewaters polluted biological degradation. However, using conventional treatment methods could not effectively degrade and mineralize of organic dyes [1, 2]. Due to generating physical and chemical effects, such as promoting the mass transfer and active radical formation, sonication can be employed for process intensification in numerous fields, including catalysis. Ultrasound, that is, sound waves of frequency above 20 kHz, can benefit catalysis in multiple ways, from enhacing the synthesis of photocatalysts with tailored physicochemical properties to improving reaction efficiency via synergisms between ultrasound and light irradiation in sonophotocatalysis [3, 4]. In recent years, the application of ultrasound has considered as a promising external field-enhanced catalytic technology that can significantly promote the efficiency of both downhill and uphill reactions[5, 6] . Sonocatalyst has widely used as an advanced oxidation process (AOP) for water and wastewater treatment because of its high efficiency and simple operation [7]. However, application by only ultrasonic show a low rate for degradation organic contaminants using a lot of energy and time for an incomplete removal process, unless using sonocatalysts which are active under ultrasonic irradiation resulting in accelerate •OH forming [8]. Various catalysts such as CuS, TiO_2, $ZnTiO_3$, Er doped ZnO have exposed high sonocatalytic activities [9, 10]. However, there is a need for developing new magnetic composite sonocatalysts with high catalytic activity. Photocatalytic and sonocatalytic processes show the same creating electron–hole pairs on the surface of catalyst [11].

Gratiphic carbon (g-C_3N_4) is considered to be the most stable allotrope among various carbon nitrides under ambient conditions. The proposed structure of g-C_3N_4 is two-dimensional frameworks of tri-s-triazine connected via tertiary amines, which makes it possess high stable thermal (up to 600 °C in air) and chemical stability (against acid, base, and organic solvents) [12]. Because of their unique size- and morphology-dependent physical and chemical properties, Fe_3O_4 nanoparticle have paid more attention by world-wide researcher for their potential applications as magnetic storage, biosensors, communication materials, magnetic resonance imaging [13]. The controlled synthesis processes of Fe_3O_4 NPs to deliver a desired structure, composition, and shape control made them be used in various promising applications.

In recent years, loading the catalysts with magnetic materials has been used as a new approach for enhancing catalytic activity, magnetic and antiphotocorrosion characteristics for effective recovery and reuse [14, 15]. In the present study, application the magnetic Fe_3O_4 cluster spheres/g-C_3N_4 applied as a new sonocatalyst for an efficient H_2O_2-assisted sonodegradation of three organic dyes in aqueous solutions were reported. This sonocatalyst composite was synthesized via simple hydrothermal method. Methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) were employed as organic dye models for evaluating sonocatalytic activity of pure Fe_3O_4 cluster spheres, g-C_3N_4 and Fe_3O_4 cluster spheres/g-C_3N_4.

2. Experimental

2.1. Synthesis of composites

Pure g-C_3N_4 powder was prepared using melamine as a precursor at 550 ^{0}C for 4h in a muffle furnace. The obtained products were washed several times with de-ionized water then grounded for further use. The Fe_3O_4/g-C_3N_4 composite was prepared by simple hydrothermal method. In a typical procedure, a certain amount of g-C_3N_4 (0.5g) and $Fe(NO_3)_3 \cdot 9H_2O$ (2.04 g) were dissolved in 60ml of deionized water under magnetic stirring. The solution was put into a Teflon-lined autoclave, followed by adding with 10 mL of sodium alginate solution (10 g/L), and 10 ml KOH (2M). After 30 min ultrasonic treatment, the mixture was transfered into a Teflon liner of 100mL capability. The autoclave was sealed and heated at 180°C for 12h and cooled to room temperature naturally. The resulting precipitant was recovered by filtration, followed by washing with distilled water three times, and drying at 80°C for 10h.

2.2. Characterization

X-ray diffraction (XRD analysis was carried out an X-ray powder diffractometer with Cu Kα radiation at 40 kV and 40 mA. The morphology and internal structure of the prepared samples were further checked by transmission electron microscopy (FESEM), using a JEM 2100F electron microscope operated at a voltage of 200 kV. UV–vis reflectance spectra of the powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using an RSAPE-20 reflectance spectroscopy accessory (Labsphere Inc., NorthSutton, NH). The PL spectra of products were measured by a transient fluorescence spectrometer (Shimadzu RF-5301PC).

2.3. The sonocatalytic degradation

The sonocatalytic degradation experiments were carried out by measuring the decoloration of dyes solution. RhB, MB, MO were used as the model pollutant to evaluate the sonodegradation activity of the Fe_3O_4/gC_3N_4 composites. In a typical process, 0.1 g of Fe_3O_4/gC_3N_4 composite was added into 50 mL of the dye (10mg/L) aqueous solution with countinuous stirring. Then 0.1ml of the H_2O_2 aqueous solution (30%) was added to the reaction solution. The mixed solution was then placed inside an a EYG-3003 bath with the frequency fixed at 40 kHz and temperature range controlled from 25 to 28 °C. About 5ml of the suspension were collected after a defined time and centrifuged to remove the catalyst for UV-vis spectrum measurement.

3. Result and Discussion

3.1. XRD analysis

Fig.1 shows X-ray diffaction pattens of g-C_3N_4, Fe_3O_4 and Fe_3O_4 clusters/gC_3N_4 20% wt. The patterns showed the sharp and intense peaks indicating the photocatalysts were well crystallized. As shown in the Fig. 1, all the diffraction peaks and position of pure Fe_3O_4 and Fe_3O_4 clusters/gC_3N_4 composite can be indexed to the cubic Fe_3O_4 (JCPDS 86-1354). The strong and sharp diffraction peaks signify exbihite the high crystallinity of Fe_3O_4 cluster microspheres [16]. The two characteristic peaks of g-C_3N_4 at 13.28 and 27.33 can be indexed to (100) and (002) diffraction planes (JCPDS 87-1526). Compared to pure g-C_3N_4, it can be seen clearly most peaks for Fe_3O_4/g-C_3N_4 indexing to the structure of Fe_3O_4. The character of g-C_3N_4 could not be exposed in the XRD pattern of Fe_3O_4/g-C_3N_4 composite sample could be attributed by the low adding content and well dispersion of g-C_3N_4 powders. However, g-C_3N_4 can still be found in the composites due of the appearance of the peak at 26.5^0. The results suggests the composites were formed between g-C_3N_4 and Fe_3O_4 cluster spheres.

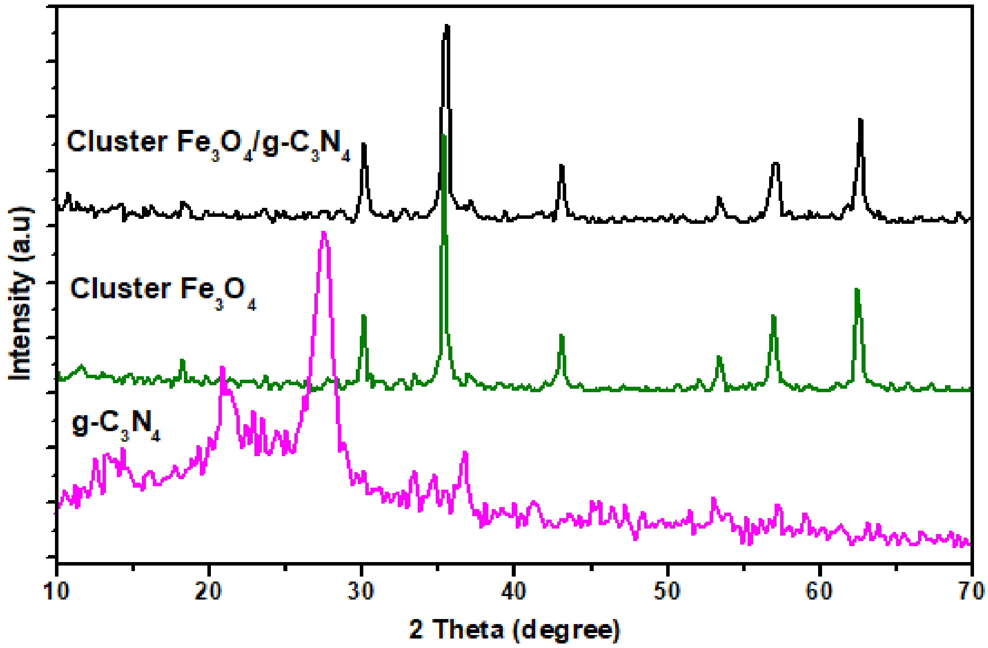

Fig. 1. XRD pattern of g-C_3N_4, Fe_3O_4 and Fe_3O_4/gC_3N_4

3.2. SEM analysis

The surface properties of pure cluster sphere Fe_3O_4 and Fe_3O_4 clusrter spheres/g-C_3N_4 composite catalyst was observed using SEM method. The obtained results are shown in Fig. 2. As depicted in Fig. 2a, the as-prepared product is composed of a large quantity of well-dispersed microspherical particles. These particles have uniform size and shape, most of which are spheres of 300-500 nm. In addition, the SEM image of spherical particles reveal that these Fe_3O_4 particles are colloidal nanocrystal clusters with a hierarchical architecture, and were built up from many single crystallites of approximately 30-40 nm in size. The average crystallite size observed from the SEM image, which are consistent with the calculation result from the XRD pattern. In particular, it can be seen products are composed of nanocrystal pieces by the ordered assembly. As depicted in Fig. 2b, the characteristic lamellar layered and planar structure can be obtained for the pure g-C_3N_4 . From Fig. 2c, it is seen that when Fe_3O_4 clusters were modified with the g-C_3N_4, the surface of the samples became less rough. It can be attributed to covering the surface of Fe_3O_4 by g-C_3N_4 particles. The accommodation of g-C_3N_4 on the surface of Fe_3O_4 lead to the formation of a tight heterostructure. In this case, two phases of g-C_3N_4 and Fe_3O_4 are clearly seen and close contact to form an intimate interface [17-19]. It is found that cavitations created in sonochemical technique play an important role in the preparation of heterostructure materials. This can promote the formation of the stable hybrid structure between g-C_3N_4 and Fe_3O_4 composite [20].

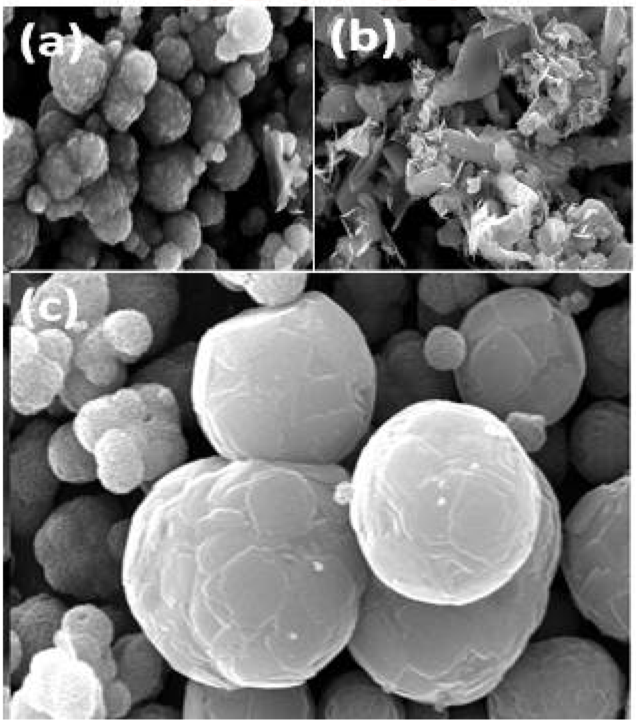

Fig. 2. SEM image of Fe_3O_4 cluster spheres (a); g-C3N4 (b), and Fe_3O_4/g-C_3N_4 composites (c)

3.3. Sonocatalytic degradation of dye

The sonocatalytic activity of the Fe_3O_4/g-C_3N_4 catalysts were evaluated through the degradation of RhB, MB, MO in the presence of H_2O_2 with ultrasonic irradiation. The results of sonocatalytic activities of the samples prepared at different conditions are shown in Fig. 3. No dye degradation can be observed without catalytic. The sonocatalytic activity of the cluster Fe_3O_4/g-C_3N_4 composite are further examinated by comparison with that of pure two-component. Compared with sonolysis/H_2O_2, the higher degradation of dyes were achieved via sonocatalytic process. The degradation efficiency of sonolysis/H_2O_2, sonocatalysis using g-C_3N_4/H_2O_2, Fe_3O_4/H_2O_2, Fe_3O_4/g-C_3N_4/H_2O_2 systems was 3%, 64%, 22 % and 96.5% within reaction time of 150 min for RhB, respectively. Cluster Fe_3O_4/g-C_3N_4 composite show much more efficient than pure cluster sphere Fe_3O_4 and pure g-C_3N_4 (Fig. 3a). The sonocatalytic processes for MB and MO degradation show the same results as depicted in Fig. 3b and Fig. 3c.

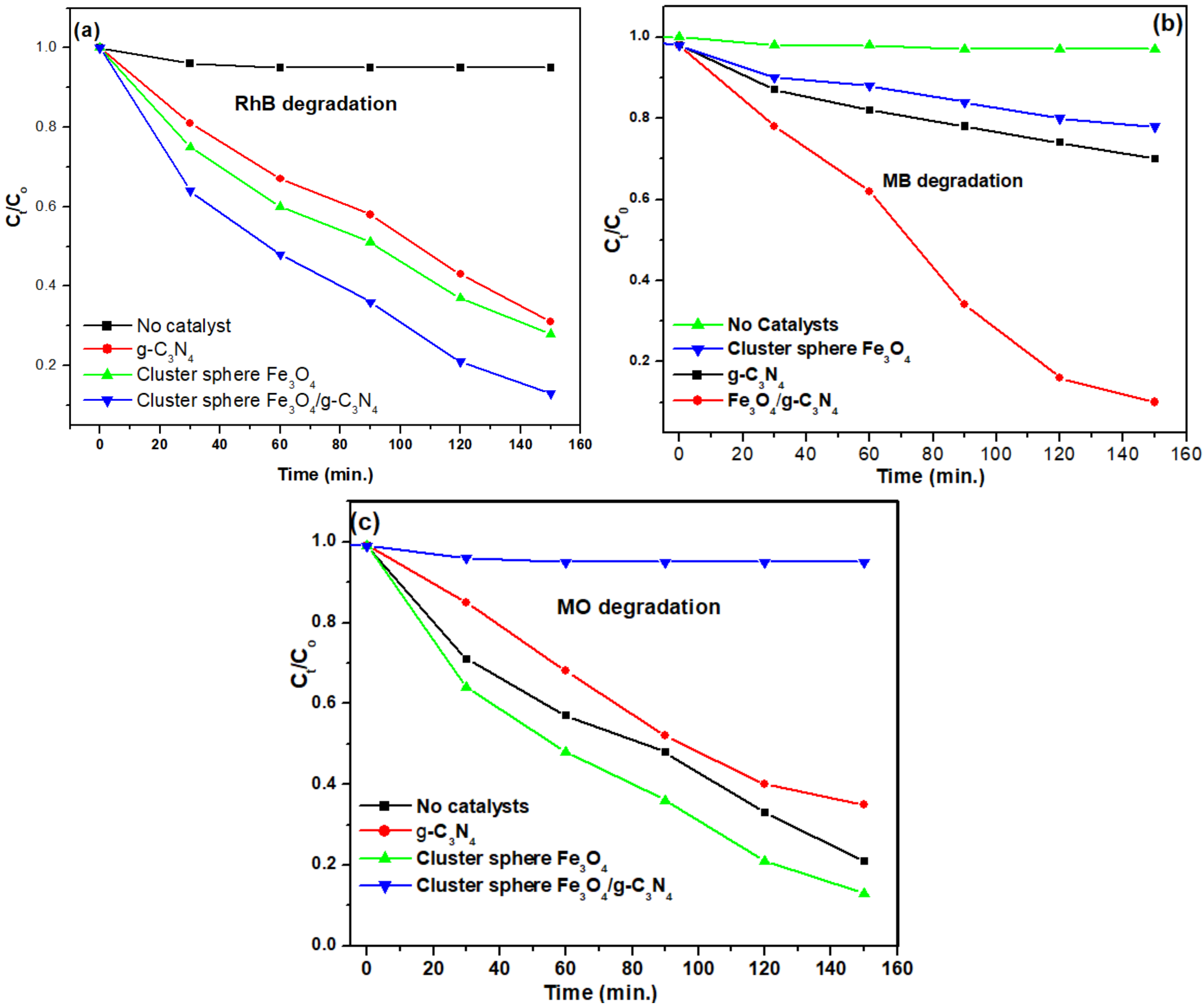

Fig. 3. The dye sono-degradation with different catalysts: (a) RhB degradation; (b) MB degradation; (c) MO degradation

The excellent sonocatalytic activity of cluster sphere Fe_3O_4/g-C_3N_4 composite can be ascribed to their high crystalline, morphology and hibrid structure. The chemical effect of sonolysis eventuates in a phenomena known as the acoustic cavitation that involves generation, growth and collapse of the microbubbles that are created as a result of ultrasound crossing through the aquatic medium [21]. The final outcome of this process is the fabrication hot spots that exposes high pressure and temperature on the catalyst surface. These hot spots result in the appropriate conditions to active and dissociate H_2O molecules. As the result, the strong oxidizing agents and the •OH reactive radicals are formed continuously [22]. The accelerating impact of the heterogeneous catalyst could be explained by the synergy effect between the ultrasonic irradiation and the catalyst. Therefore, these composites with a hybrid structure would result in an electric field at the interface, then improving the sonocatalytic activity.

To investigate the stability of the Fe_3O_4/g-C_3N_4 composites, the recycle tests were conducted in the oxidation process under ultrasonic irradiation. The results reveal that the as-obtained composite was easily collected by an internal magnet and dyes removal effective has no significant change during the 4th successive cycles, indicating the high stability of the composite (Fig. 5). The chracteristic plays a very important role in application for water treatment at industry scale. The high sonocatalytic activity, the stability and the easily separation suggest that the Fe_3O_4/g-C_3N_4 can be promising candidates for the dyes removal application.

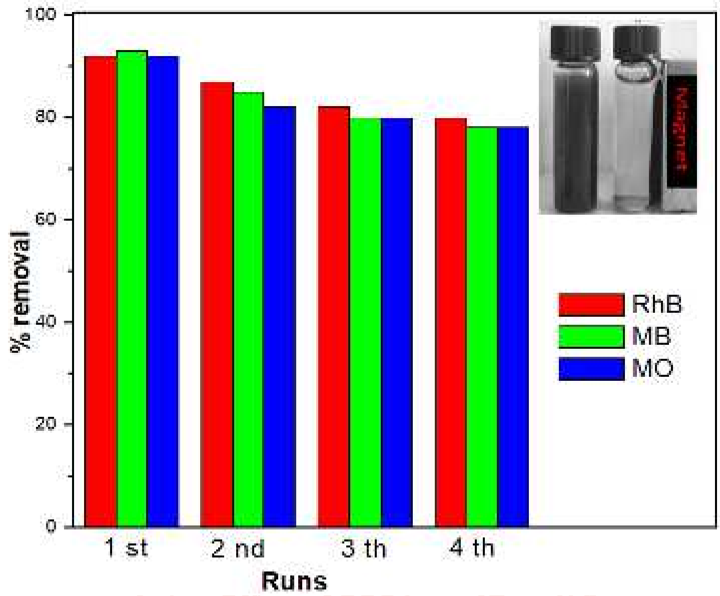

Fig. 5. The stability of the Bi/g-C_3N_4 composites after 4 recycles

4. Conclusion

Magnetic separable Fe_3O_4/g-C_3N_4 composite was successfully prepared by simple hydrothermal process. The results showed that Fe_3O_4/g-C_3N_4 composite with added 20% g-C_3N_4 revealed the high sonocatalytic activity for RhB, MB and MO degradation. The improved sonocatalytic activity of as-prepared Fe_3O_4/g-C_3N_4 can be ascribed to their mophology and hibrid structure. The structure of g-C_3N_4 and Fe_3O_4 is suitable for adsorption ultrasonic while comparing to a physical mixture of two-component. In addition, these composites with a hybrid structure would form an flexible electric field at the interface, then improving the sonocatalytic activity. On other hand, the integration of H_2O_2 and catalyst dosage also are factor that enhacing the sonocatalytic degradation of dyes. Specially, Fe_3O_4/g-C_3N_4 can be collected easily by using an external magnetic field and exposed the high stability after 4 recycles. These properties of the Fe_3O_4 cluster sphere/g-C_3N_4 composites could be a promising sonocatalyst for the degradation dye contaminants.

Reference

[1] S.S.I. Alamri Rahmah Dhahawi Ahmad, Rohana Adnan, Wen Da Oh , Ahmad Faiz Abdul Lati , Alomari Asma Dhahawi Ahmad, Fenton degradation of ofloxacin antibiotic using calcium alginate beads impregnated with Fe3O4-montmorillonite composite, International Journal of Biological Macromolecules 229 (2022) 838-848.

[2] E. Bartfai, K. Nemeth, B.E. Mrabate, M. Udayakumar, K. Hernadi, Z. Nemeth, Synthesis, Characterization and Photocatalytic Efficiency of ZnO/MWCNT Nanocomposites Prepared Under Different Solvent Conditions, J Nanosci Nanotechnol, 19 (2019) 422-428.

[3] Z. Cheng, X. Quan, Y. Xiong, L. Yang, Y. Huang, Synergistic degradation of methyl orange in an ultrasound intensified photocatalytic reactor, Ultrason Sonochem, 19 (2012) 1027-1032.

[4] Y.C. Chen, A.V. Vorontsov, P.G. Smirniotis, Enhanced photocatalytic degradation of dimethyl methylphosphonate in the presence of low-frequency ultrasound, Photochem Photobiol Sci, 2 (2003) 694-698.

[5] M. Eghbali-Arani, A. Sobhani-Nasab, M. Rahimi-Nasrabadi, F. Ahmadi, S. Pourmasoud, Ultrasound-assisted synthesis of YbVO4 nanostructure and YbVO4/CuWO4 nanocomposites for enhanced photocatalytic degradation of organic dyes under visible light, Ultrason Sonochem, 43 (2018) 120-135.

[6] P. Gholami, L. Dinpazhoh, A. Khataee, A. Hassani, A. Bhatnagar, Facile hydrothermal synthesis of novel Fe-Cu layered double hydroxide/biochar nanocomposite with enhanced sonocatalytic activity for degradation of cefazolin sodium, J Hazard Mater, 381 (2020) 120742.

[7] V. Ramasamy Raja, D. Rani Rosaline, A. Suganthi, M. Rajarajan, Ultrasonic assisted synthesis with enhanced visible-light photocatalytic activity of NiO/Ag_3VO_4 nanocomposite and its antibacterial activity, Ultrason Sonochem, 44 (2018) 73-85.

[8] S.Y. Hao, Y.H. Li, J. Zhu, G.H. Cui, Structures, luminescence and photocatalytic properties of two nanostructured cadmium(II) coordination polymers synthesized by sonochemical process, Ultrason Sonochem, 40 (2018) 68-77.

[9] H. Eskandarloo, A. Badiei, M.A. Behnajady, A. Tavakoli, G.M. Ziarani, Ultrasonic-assisted synthesis of Ce doped cubic-hexagonal ZnTiO3 with highly efficient sonocatalytic activity, Ultrason Sonochem, 29 (2016) 258-269.

[10] H. Gao, W. Liu, B. Lu, F. Liu, Photocatalytic activity of La, Y Co-doped TiO2 nanoparticles synthesized by ultrasonic assisted sol-gel method, J Nanosci Nanotechnol, 12 (2012) 3959-3965.

[11] M. Ahmad, E. Ahmed, Z.L. Hong, W. Ahmed, A. Elhissi, N.R. Khalid, Photocatalytic, sonocatalytic and sonophotocatalytic degradation of Rhodamine B using ZnO/CNTs composites photocatalysts, Ultrason Sonochem, 21 (2014) 761-773.

[12] D.L. Shun Wang, Zhaojie Wang, Nuo Yu, Haifeng Wang, Zhigang Chen, Lisha Zhang, Synthesis of ultrathin g-C3N4/graphene nanocomposites with excellent visible-light photocatalytic performances, Functional Materials LettersVol. 12, No. 03, 1950025 (2019), 12 (2019) 1950025-1950029.

[13] P. Alimard, Fabrication and kinetic study of Nd-Ce doped Fe3O4-chitosan nanocomposite as catalyst in Fenton dye degradation, Polyhedron, 171 (2019) 98-107.

[14] W. He, Z. Li, S. Lv, M. Niu, W. Zhou, J. Li, R. Lu, H. Gao, C. Pan, S. Zhang, Facile synthesis of Fe3O4@MIL-100(Fe) towards enhancing photo-Fenton like degradation of levofloxacin via a synergistic effect between Fe3O4 and MIL-100(Fe), Chemical Engineering Journal, 409 (2021) 128274.

[15] N. Zhang, X. Li, Y. Wang, B. Zhu, J. Yang, Fabrication of magnetically recoverable Fe3O4/CdS/g-C3N4 photocatalysts for effective degradation of ciprofloxacin under visible light, Ceramics International, 46 (2020) 20974-20984.

[16] D. Beketova, M. Motola, H. Sopha, J. Michalicka, V. Cicmancova, F. Dvorak, L. Hromadko, B. Frumarova, M. Stoica, J.M. Macak, One-Step Decoration of TiO2 Nanotubes with Fe3O4 Nanoparticles: Synthesis and Photocatalytic and Magnetic Properties, ACS Applied Nano Materials, 3 (2020) 1553-1563.

[17] X. Wang, W. Mao, J. Zhang, Y. Han, C. Quan, Q. Zhang, T. Yang, J. Yang, X. Li, W. Huang, Facile fabrication of highly efficient g-C(3)N(4)/BiFeO(3) nanocomposites with enhanced visible light photocatalytic activities, J Colloid Interface Sci, 448 (2015) 17-23.

[18] T.S. Ahooie, N. Azizi, I. Yavari, M.M. Hashemi, Magnetically separable and recyclable g-C3N4 nanocomposite catalyzed one-pot synthesis of substituted imidazoles, Journal of the Iranian Chemical Society, 15 (2018) 855-862.

[19] K. Vignesh, A. Suganthi, B.-K. Min, M. Kang, Photocatalytic activity of magnetically recoverable MnFe2O4/g-C3N4/TiO2 nanocomposite under simulated solar light irradiation, Journal of Molecular Catalysis A: Chemical, 395 (2014) 373-383.

[20] M. Masjedi-Arani, M. Salavati-Niasari, Cd2SiO4/Graphene nanocomposite: Ultrasonic assisted synthesis, characterization and electrochemical hydrogen storage application, Ultrason Sonochem, 43 (2018) 136-145.

[21] R. Mahdavi, S.S. Ashraf Talesh, Enhanced selective photocatalytic and sonocatalytic degradation in mixed dye aqueous solution by ZnO/GO nanocomposites: Response surface methodology, Materials Chemistry and Physics, 267 (2021) 124581.

[22] L. Xu, X.-F. Wang, B. Liu, T. Sun, X. Wang, Fabrication of ferrous tungstate with enhanced sonocatalytic performance for meloxicam removal, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 627 (2021) 127222.